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(54) COMPOSITION AQUEUSE GELIFIABLE A GELIFICATION DIFFEREE

(54) AQUEOUS GELLABLE COMPOSITION WITH DELAYED GELLING TIME

(57)

An aqueous gellable composition for use to modify the permeability of high-permeability regions in petroleum reservoirs, wherein the aqueous gellable composition containing an organic, water-soluble polymer crosslinkable with chrome ion and a crosslinking and gel-retarding system definable by the formula: $Cr(L)_m.nL'$ L' being in form not complexed with chrome ion wherein: Cr is a trivalent chrome ion; L is an organic ligand consisting of a monocarboxylate or dicarboxylate ion, optionally bearing one or more amino or hydroxy functional group(s), in form complexed with chrome ion; is an organic ligand selected among malonic and ascorbic acids or when L' is salicylic acid, L is selected among: acetate, propionate, butyrate, malonate, succinate, glutarate, adipate, glycolate, lactate, alpha-hydroxybutyrate, ascorbate, tartrate, alpha-aminoacetate (glycine) and alpha-amino-beta-hydroxypropionate (serine), alpha-aminobutyrate, phthalate; in form complexed with chromium ion; has a value comprised within the range of from 1 to 3, depending on the nature of the ligand L; has a value comprised within the range of from 0.5 to 100; with the proviso that in the crosslinking and gel-retarding system, the ligand L is different from the ligand L'.



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(54) Title: AQUEOUS GELLABLE COMPOSITION WITH DELAYED GELLING TIME

(57) Abrégé/Abstract:

An aqueous gellable composition for use to modify the permeability of high-permeability regions in petroleum reservoirs, wherein the aqueous gellable composition containing an organic, water-soluble polymer crosslinkable with chrome ion and a crosslinking and gel-retarding system definable by the formula: $Cr(L)_m nL'$ L' being in form not complexed with chrome ion wherein: Cr is a trivalent chrome ion; L is an organic ligand consisting of a monocarboxylate or dicarboxylate ion, optionally bearing one or more amino or hydroxy functional group(s), in form complexed with chrome ion; L' is an organic ligand selected among malonic and ascorbic acids or when L' is salicylic acid, L is selected among: acetate, propionate, butyrate, malonate, succinate, glutarate, adipate, glycolate, lactate, alpha-hydroxybutyrate, ascorbate, tartrate, alpha-aminoacetate (glycine) and alpha-amino-beta-hydroxypropionate (serine), alpha-aminobutyrate, phthalate; in form complexed with chromium ion; m has a value comprised within the range of from 1 to 3, depending on the nature of the ligand L; n has a value comprised within the range of from 0.5 to 100; with the proviso that in the crosslinking and gel-retarding system, the ligand L is different from the ligand L'.

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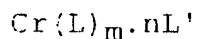
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ABSTRACT

An aqueous gellable composition for use to modify the permeability of high-permeability regions in petroleum reservoirs, wherein the aqueous gellable composition containing an organic, water-soluble polymer crosslinkable with chrome ion and a crosslinking and gel-retarding system definable by the formula:



L' being in form not complexed with chrome ion
wherein:

Cr is a trivalent chrome ion;

L is an organic ligand consisting of a monocarboxylate or dicarboxylate ion, optionally bearing one or more amino or hydroxy functional group(s), in form complexed with chrome ion;

L' is an organic ligand selected among malonic and ascorbic acids or when L' is salicylic acid, L is selected among: acetate, propionate, butyrate, malonate, succinate, glutarate, adipate, glycolate, lactate, alpha-hydroxybutyrate, ascorbate, tartrate, alpha-aminoacetate (glycine) and alpha-amino-beta-hydroxypropionate (serine), alpha-aminobutyrate, phthalate; in form complexed with chromium ion;

m has a value comprised within the range of from 1 to 3, depending on the nature of the ligand L;

n has a value comprised within the range of from 0.5 to 100;

with the proviso that in the crosslinking and gel-retarding system, the ligand L is different from the ligand L'.

"AQUEOUS GELLABLE COMPOSITION WITH DELAYED GELLING TIME"

The present invention relates to an aqueous gellable composition having a delayed gelling time within wide time and temperature ranges, useful to modify the permeability of high-permeability regions in petroleum reservoirs, in particular high-temperature petroleum reservoirs.

The invention relates also to a process for reducing the permeability of a reservoir, which process uses said gellable composition.

It is well-known that at the end of the primary step of recovery of petroleum from a petroleum reservoir, in which step the recovery occurs thanks to the natural energy stored in the petroleum reservoir, or with the use of mechanical energy, inside the reservoir still a large amount of petroleum remains. Therefore, in order to increase the amount of petroleum which can be extracted, techniques of secondary recovery are customarily used, which essentially consist in injecting into the reservoir a fluid, generally water or an aqueous polymeric solution, or a gas, such as carbon dioxide or steam, which conveys petroleum to the production well.

However, owing to the heterogeneity of the petroleum bearing rock, which is constituted by regions with different permeability, such fluids tend to preferentially flow through the higher-permeability regions. The low-permeability regions remain hence non-fluxed, or only partially fluxed, and this matter of fact prevents the extraction of the therein contained petroleum.

A proposal of solution to overcome such a problem

consists in modifying the permeability of the reservoir either completely or partially occluding the high-permeability regions, so that the flow of the fluid subsequently injected into the reservoir for the recovery of petroleum can be diverted towards the low-permeability regions.

For that purpose, one may resort to the injection into the reservoir of an aqueous solution of a gellable polymer, which can be gelled by means of a multivalent metal ion, so as to cause polymeric gels to be generated in situ.

In particular, the use is known in the art, of gellable compositions having delayed gelling time, which compositions generally consist of a crosslinkable polymer, such as, e.g., a polyacrylamide, a multivalent metal ion, and a ligand or sequestering agent for said multivalent metal ion. For example, in European Patent Applrs. Public. No. 0 390 279 and No. 0 390 282, the use is disclosed of compositions which can be gelled by means of trivalent chrome, which compositions contain, as the retardant agent, an organic ligand selected from the group consisting of the aliphatic or aromatic dicarboxy acids, or from the group consisting of the alpha-hydroxyacids or alpha-aminoacids.

In UK patent application 2,187,773, a gellable composition having a delayed gelling time is disclosed, which contains a water-soluble polymer, a crosslinking agent constituted by a complex of trivalent chrome with a carboxylate ion, in particular acetate ion, and a retardant agent, generally constituted by acetic acid.

Unfortunately, such compositions known from the

prior art allow delayed gelling times to be obtained, which are generally unsatisfactory for practical uses. In particular, the compositions known from the prior art are, in general, unsatisfactory when they are used to occlude large regions of a reservoir and/or regions far away from the injection well, in particular when reservoirs are processed which display high temperatures of their own, which accelerate the gelling rate, with the risk of a premature gel formation, and consequent occlusion of undesired regions.

Therefore, a purpose of the present invention is overcoming the drawbacks which affect the prior art, by means of an aqueous gellable composition, with delayed gelling time, which gelling time can be preset within wide ranges of time and temperature, useful to modify the permeability of high-permeability regions in petroleum reservoirs, in particular high-temperature reservoirs.

Another purpose of the present invention is a process for reducing the permeability of a petroleum reservoir, which process uses said composition.

Other purposes of the invention will be evident from the following disclosure and experimental examples.

In particular, the present Applicant found, according to the present invention, that some systems, which comprises two carboxylate ligands different from each other, with the first ligand being complexed with trivalent chrome ion, and the second ligand being in free form, lead to unexpectedly good results when they are used as crosslinking and gel-retarding systems in converting gellable organic polymers into gels. In particular, these unexpectedly good results consist in that the delayed

gelling time and temperature can be preset within wide ranges, as a function of the particular pair of selected ligands, and of their mutual ratio in the cross-linking and gel-retarding system.

In accordance therewith, according to a first aspect thereof, the present invention relates to an aqueous gellable composition, containing an organic, water-soluble polymer crosslinkable with chrome ion and a crosslinking and gel-retarding system definable by the formula:



L' being in form not complexed with chrome ion
wherein:

Cr is a trivalent chrome ion;

L is an organic ligand consisting of a monocarboxylate or dicarboxylate ion, optionally bearing one or more amino or hydroxy functional group(s), in form complexed with chrome ion;

20 L' is an organic ligand selected among malonic and ascorbic acids or when L' is salicylic acid, L is selected among: acetate, propionate, butyrate, malonate, succinate, glutarate, adipate, glycolate, lactate, alpha-hydroxybutyrate, ascorbate, tartrate, alpha-aminoacetate (glycine) and alpha-amino-beta-hydroxypropionate (serine), alpha-aminobutyrate, phthalate; in form complexed with chromium ion;

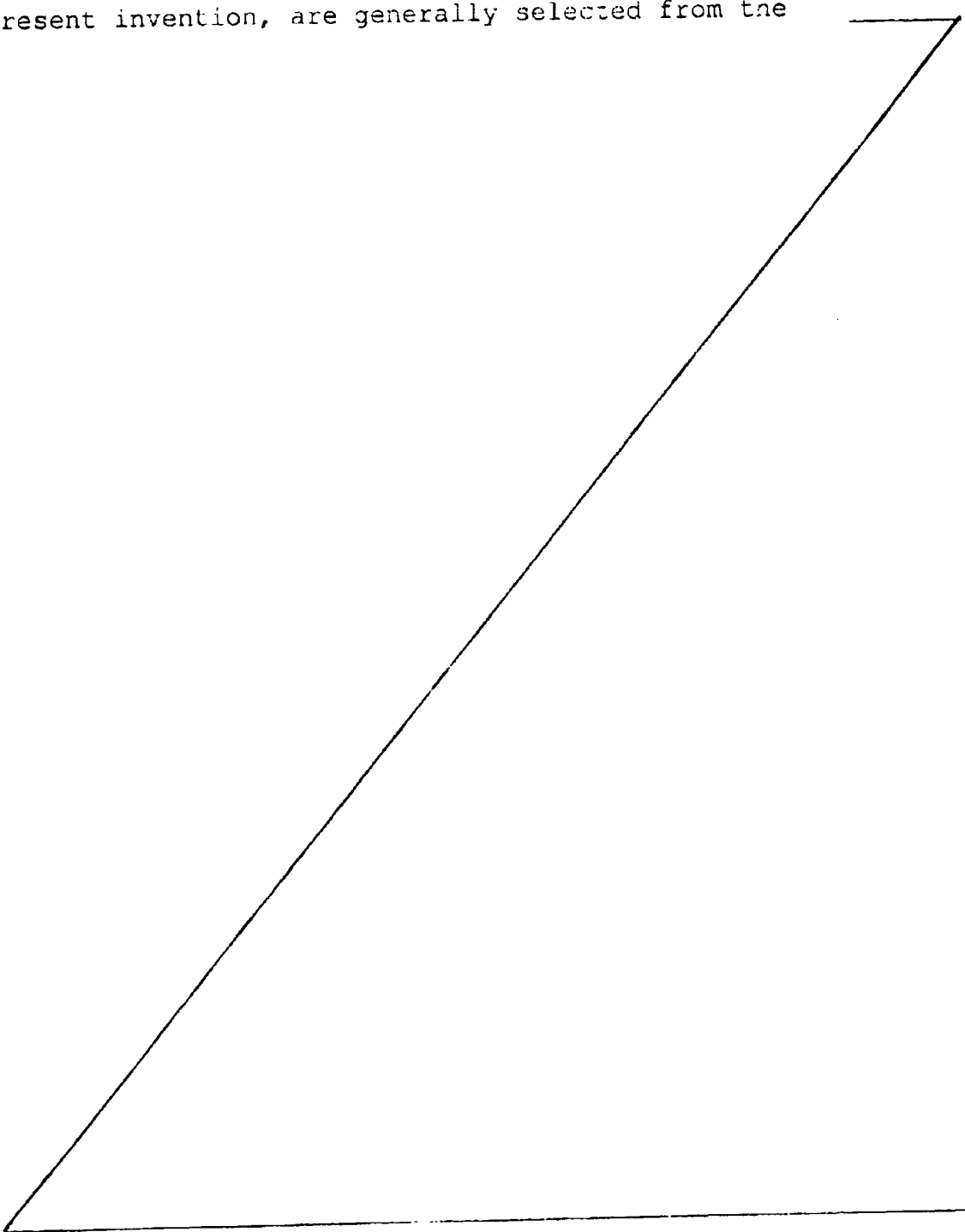
m has a value comprised within the range of from 1 to 3, depending on the nature of the ligand L;

n has a value comprised within the range of from 0.5 to 100;

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with the proviso that in the crosslinking and gel-retarding system, the ligand L is different from the ligand L'.

The water-soluble organic polymers which can be crosslinked with chrome ion, useful for the purposes of the present invention, are generally selected from the



group consisting of acrylamide polymers. In particular, there can be used either acrylamide homopolymers, or acrylamide copolymers with one or more copolymerisable unsaturated monomer(s), such as, e.g., acrylic acid, methacrylamide, sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone. Among the copolymers, the copolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate, the copolymers of acrylamide with N-vinyl-2-pyrrolidone and the terpolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone are preferably used.

Said acrylamide polymers and copolymers can be either substantially non-hydrolysed (less than 1% of amidic groups hydrolysed into free carboxy groups), or partially hydrolysed (more than 1% of amidic groups hydrolysed into free carboxy groups).

The molecular weight of these acrylamide(co)polymers may generally be comprised within the range of from 100,000 to 20,000,000, and, preferably, within the range of from 200,000 to 12,000,000.

The concentration of the acrylamide (co)polymer in the gellable composition according to the present invention can generally range from 1,000 to 80,000 ppm (parts per million parts by weight), and preferably will be comprised within the range of from 3,000 to 50,000 ppm and, in the most preferred form of practical embodiment, will be comprised within the range of from 5,000 to 10,000 ppm when fresh water is used, and of from 10,000 to 30,000 when salt water is used (such as, e.g., sea water).

The ligand L and the ligand L' of the

crosslinking and gel-retarding system according to the present invention can be selected from among:

- monocarboxy aliphatic acids $R\text{-COOH}$, wherein R is a $C_1\text{-}C_6$ alkyl radical; examples of aliphatic monocarboxy acids are: acetic acid, propionic acid and butyric acid;
- dicarboxy aliphatic acids $\text{HOOC-(CH}_2\text{)}_a\text{-COOH}$, wherein a has a value comprised within the range of from 0 to 4, and their relevant monoesters and monoamides; examples of such aliphatic dicarboxy acids and relevant monoesters and monoamides are: malonic acid, succinic acid, glutaric acid and adipic acid;
- aliphatic alpha-hydroxyacids $R'\text{-CH(OH)-COOH}$, in which R' is a hydrogen atom, or an alkyl or hydroxyalkyl radical containing from 1 to 6 carbon atoms in its alkyl or hydroxyalkyl moiety, and the lactones thereof; examples of such aliphatic alpha-hydroxyacids and relevant lactones are: glycolic acid, lactic acid, alpha-hydroxybutyric acid, ascorbic acid and tartaric acid;
- aliphatic alpha-aminoacids $R''\text{-CH(NH}_2\text{)-COOH}$, wherein R'' is a hydrogen atom, or an alkyl or hydroxyalkyl radical containing from 1 to 6 carbon atoms in its alkyl or hydroxyalkyl moiety; examples of such aliphatic alpha-aminoacids are: glycine, alpha-aminobutyric acid and serine;
- aromatic alpha-dicarboxy acids, such as, e.g., phthalic acid; and
- aromatic alpha-hydroxyacids, such as, e.g., salicylic acid.

According to a preferred form of practical embodiment of the present invention, said ligands L is acetate ion or malonate ion or glycolate ion and the ligand

L' is selected from among: malonic acid, ascorbic acid, glycolic acid, alpha-hydroxybutyric acid, alpha-aminobutyric acid, serine, phthalic acid and monoamine of glutaric acid.

Particularly preferred crosslinking/retardant systems according to the present invention are:

- $\text{Cr}(\text{acetate})_3 \cdot n$ malonic acid,
with n comprised within the range of from 0.5 to 100;
- $\text{Cr}(\text{acetate})_3 \cdot n$ salycilic acid,
10 with n comprised within the range of from 0.5 to 50;
- $\text{Cr}(\text{acetate})_3 \cdot n$ ascorbic acid,
with n comprised within the range of from 0.5 to 100;
- $\text{Cr}(\text{malonate})_3 \cdot n$ salycilic acid,
with n comprised within the range of from 0.5 to 50;
- $\text{Cr}(\text{glycolate})_3 \cdot n$ malonic acid,
with n comprised within the range of from 0.5 to 100;
and
- $\text{Cr}(\text{malonate})_3 \cdot n$ glycolic acid,
with n comprised within the range of from 0.5 to 100.

20 The crosslinking and gel-retarding system according to the present invention can additionally contain one or more hydroxy ions and/or neutral molecules, such as, e.g., water or pyridine, and other monovalent and divalent inorganic ions, generally Na^+ and K^+ , suitable for balancing the charge of the same system.

In the crosslinking and gel-retarding system according to the present invention, the molar ratio of the ligand L' to chrome is selected as a function of the particular pair of ligands selected and of the value of the
30 gelling delay which one wishes to obtain, also on

considering the temperature of the region of reservoir to be occluded. As indicated above, such a ratio can generally be comprised within the range of from 0.5 to 100, with preferred values ranging from 0.5 to 50.

The amount of crosslinking and gel-retarding system contained in the gellable compositions according to the present invention will be that amount which makes it possible a concentration of chrome ion to be obtained in said composition, which is comprised within the range of
10 from 10 to 5,000 ppm, and preferably within the range of from 25 to 800 ppm, with most preferred values being of from 100 to 600 ppm (parts per million parts by weight).

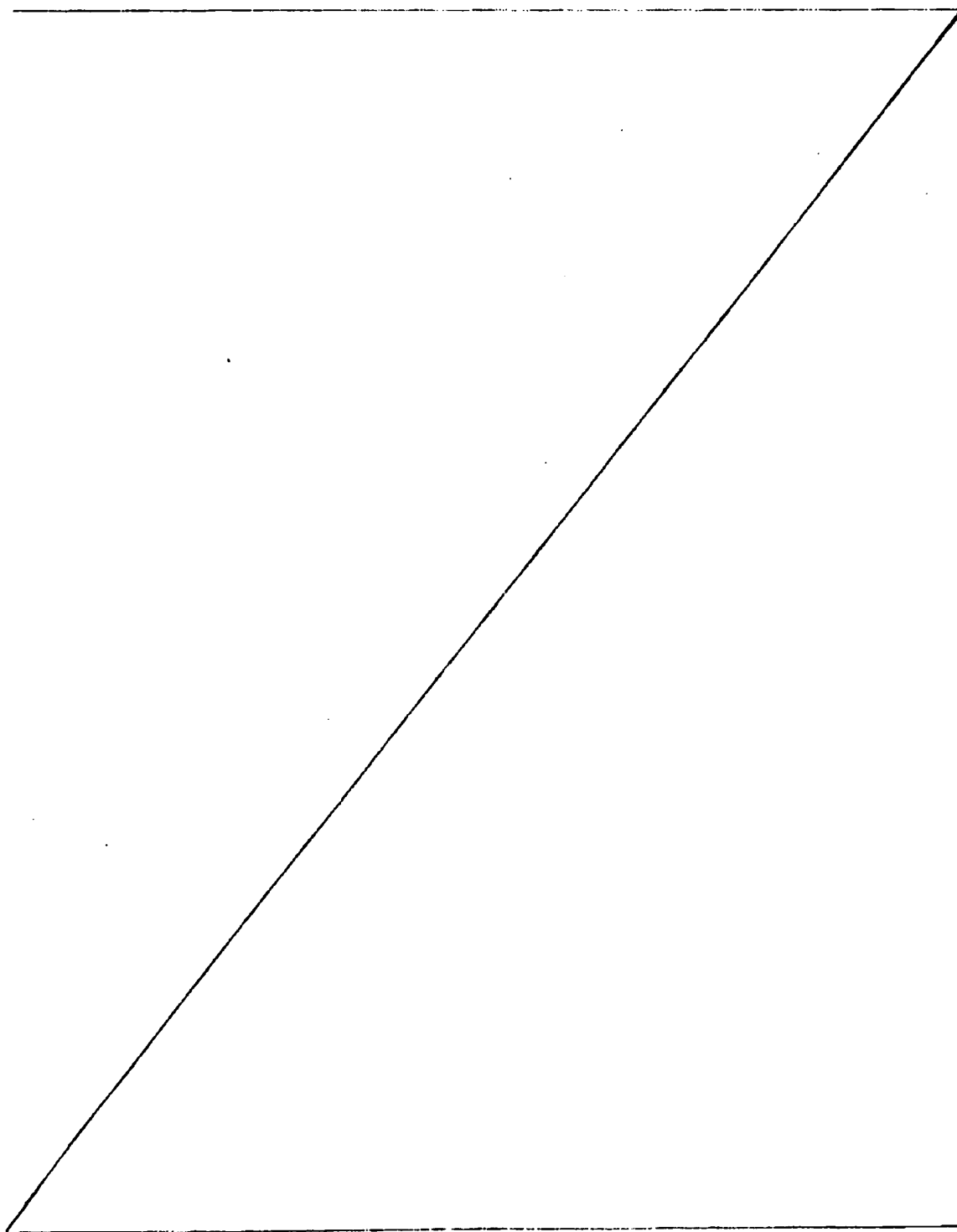
The gellable composition of the present invention can additionally contain one or more stabilizer agent(s) for the polymer, as customarily used, e.g., thiourea.

Furthermore, the gellable composition according to the present invention will have a pH value comprised within the range of gelation of the same composition, which can be comprised within the range of from about 2 to about
20 9, and preferably is of the order of from 4 to 7. Therefore, when either necessary or desired, the pH value of the composition will be adjusted by means of the addition of a mineral acid or base, as needed. A mineral acid suitable for that purpose is, e.g., hydrochloric acid, and a suitable base is, e.g., sodium hydroxide.

The aqueous gellable composition according to the present invention can be prepared by simply blending its components, on considering that the sequence of addition is not critic.

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However, preferably, an aqueous solution is prepared first, which contains the polymer and the optional stabilizer agent, then an aqueous solution of the ligand



L' is added to the solution of the polymer, and then the solution of the complex of trivalent chrome with the ligand L is added.

5 This complex can be prepared by means of known techniques, such as described, e.g., in "Inorganic Syntheses", Vol. 16, pages 80-81, and in "Comprehensive Inorganic Chemistry", Pergamon Press (Oxford), Vol. 3 (1973), pages 627-700.

10 Water used in the composition can be free from salts, or it can contain salts and, advantageously, the same water contained in the same reservoir can be used.

According to another purpose thereof, the present invention relates to a process for reducing the permeability in a petroleum reservoir, which process uses
15 the gellable composition disclosed hereinabove.

More particularly, said process comprises the following steps:

- (a) preparing an aqueous gellable composition, as disclosed hereinabove;
- 20 (b) injecting said gellable composition into the petroleum reservoir through at least one well;
- (c) causing said composition to flow through the reservoir, until it reaches and substantially fills the high-permeability region which has to be treated;
- 25 and
- (d) causing said composition to turn into a gel, with the permeability of the above said region being consequently decreased.

30 The use of the gellable composition makes it advantageously possible the permeability in high-permeability regions situated deeply in the reservoir,

where the temperature is higher, or anyway far away from the injection well, to be reduced, without that an early gelling occurs.

Thanks to the use of a free ligand and a complexed ligand, different from each other, the gelling time can be present within a very wide range, by properly selecting the pair of ligands and their mutual ratio. A further possibility of regulation of the gelling time is given by the ageing time of the complex formed by trivalent chrome ion and ligand L. More particularly, in case of acetate ion, it was found that to longer ageing times of the same complex, shorter gelling times correspond, with the other conditions being the same. In any case, it was found that the use of two different ligands in a same crosslinking and gel-retarding system is essential in order to attain the benefits of the instant invention. These benefits cannot be obtained, e.g., by using the chrome acetate/acetic acid system according to the prior art.

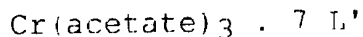
Finally, the use of two different ligands favours the selection of at least one cheap ligand, what makes it possible economic advantages to be accomplished, or a complex $\text{Cr}(\text{L})_m$ available from the market, or easy to be prepared, to be used in combination with a ligand L' , so as to accomplish good retardant performances.

The compositions according to the present invention turn into a gel with useful delayed-gelation times within a wide range of temperatures, such as from room temperature up to 120°C or more. In general, the present Applicant found that delays of up to one month, or even more, can be accomplished, by operating at temperatures of the order of from 90 to 120°C .

The invention is further illustrated by the following experimental examples.

Example 1

Use of the crosslinking and gel-retarding system:



wherein:

L' = acetic acid (for comparative purposes), monoamide of glutaric acid, phthalic acid, glycolic acid, salicylic acid or ascorbic acid.

10 In this example, as the water-soluble, gellable organic polymer, a commercial copolymer of acrylamide and sodium 2-acrylamido-2-methyl-1-propane-sulfonate in a weight ratio of approximately 72:25, with about 4% of hydrolysed amidic groups to yield carboxy groups, is used. An aqueous solution of the copolymer is prepared, and thiourea is added to it, to perform the function of stabilizer agent.

20 An aqueous solution is prepared of $\text{Cr}(\text{acetate})_3 \cdot \text{H}_2\text{O}$ complex is prepared, and the solution is allowed to age 2 days before use.

The aqueous, gellable composition are prepared by mixing, in a test tube provided with screw-threaded cap, the solution of the copolymer and stabilizer agent, with the aged aqueous solution of $\text{Cr}(\text{acetate})_3 \cdot \text{H}_2\text{O}$ complex, and subsequently adding the ligand L' (optionally as its alkali-metal salt), dissolved in water. The pH value of the resulting solution is adjusted at the value of 5 ± 0.1 , with aqueous sodium hydroxide, or aqueous hydrochloric acid, according to as needed.

30 In particular, the resulting composition contains 5,000 ppm (parts per million parts by weight) of copolymer,

5,000 ppm of thiourea and 600 ppm of trivalent chrome. The concentration of the ligand L' is, in any case, of 0.08 M (molar ratio of L'/Cr + 7:1).

The so prepared compositions are submitted to gelation by being kept in an oil bath at 120°C for 15 minutes, and being then charged to an oven at 120°C. The so obtained gelling times are reported in following Table I.

Table I

Ligand L'	Gelling time (hours)
* Acetic acid	1
* Monoamide of glutaric acid	3.3
* Phathalic acid	43
* Glycolic acid	46 - 115.5
* Salicylic acid	50
* Ascorbic acid	53 - 124

Example 2

10 Use of the crosslinking and gel-retarding system:

$$\text{Cr}(\text{CH}_3\text{COO})_3 \cdot 7 \text{ L}'$$

wherein:

L' = acetic acid (for comparative purposes), L-serine, alpha-hydroxybutyric acid, lactic acid, 2-aminobutyric acid, glycolic acid, salicylic acid, malonic aid, ascorbic acid.

20 In this example, as the water-soluble, gellable organic polymer, a commercial copolymer of acrylamide and sodium 2-acrylamido-2-methyl-1-propane-sulfonate in a weight ratio of approximately 57:43, with about 6% of amidic groups hydrolysed to yield carboxy groups, is used.

An aqueous solution of $\text{Cr}(\text{acetate})_3 \cdot \text{H}_2\text{O}$ complex is prepared, and the solution is used 1-3 days later.

By operating as in Example 1, aqueous, gellable compositions are prepared with a pH value of 5 ± 0.1 , which contain 5,000 ppm (parts per million parts by weight) of copolymer, 5,00 ppm of thiourea and 600 ppm of trivalent chrome. The concentration of the ligand L' is, in any case, of 0,08 M (molar ratio of L'/Cr = 7:1).

10 The so prepared compositions are submitted° to gelation by being kept in an oil bath at 90-95°C for 15 minutes, and being than charged to an oven at 120°C. The so obtained gelling times are reported in following Table II.

Table II

<u>Ligand L'</u>	<u>Gelling time</u>
* Acetic acid	3.8 hours
* L-serine	8-18 hours
* alpha-Hydroxybutyric acid	8-18 hours
* Lactic acid	30-45 hours
* alpha-Aminobutyric acid	26-40 hours
* Glycolic acid	48-52 hours
* Salicylic acid	3-6 days
* Malonic acid	3-6 days
* Ascorbic acid	8-9

Example 3

Use of the crosslinking and gel-retarding system:

$\text{Cr}(\text{acetate})_3 \cdot n$ malonic acid

with n comprised within the range of from 2 to 7.

By operating as in the preceding Examples, aqueous, gellable compositions are prepared with a pH value

of 5 ± 0.1 , which contain 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea and 600 ppm of trivalent chrome.

In this example, the aqueous solution of $\text{Cr}(\text{acetate})_3 \cdot \text{H}_2\text{O}$ complex is aged for 2 days.

The concentration of the ligand L' (malonic acid) in the composition is varied within the range of from 0.024 to 0.080 M, so as to have molar ratios of malonic acid/chrome comprised within the range of from 2:1 to 7:1.

10 The so prepared compositions are submitted to gelation by being kept in an oil bath at 120°C for 15 minutes, and being then charged to an oven at 120°C . The so obtained gelling times are reported in following Table III.

Table III

Concentration of malonic acid	Ratio of malonic acid: chrome	Gelling Time
0.024 M	2 : 1	22 hours
0.040 M	3.5 : 1	198 \pm 12 hours
0.056 M	5 : 1	354 \pm 24 hours
0.080 M	7 : 1	24-27 days

Example 4

Use of the crosslinking and gel-retarding system:

$\text{Cr}(\text{acetate})_3 \cdot n$ salicylic acid

with n comprised within the range of from 2 to 7.

20 By operating as in the preceding Examples, aqueous, gellable compositions are prepared with a pH value of 5 ± 0.1 , which contain 5,000 ppm (parts per million parts

by weight) of the copolymer of Example 1, 5,000 ppm of thiourea and 600 ppm of trivalent chrome.

In this example, the aqueous solution of $\text{Cr}(\text{acetate})_3 \cdot \text{H}_2\text{O}$ complex is used as soon as it is ready.

The concentration of the ligand L' (salicylic acid) in the composition is varied within the range of from 0.024 to 0.080 M, so as to have molar ratios of salicylic acid/chrome comprised within the range of from 2:1 to 7:1.

10 The so prepared compositions are submitted to gelation by being kept in an oil bath at 120°C for 15 minutes, and being then charged to an oven at 120°C. The so obtained gelling times are reported in following Table IV.

Table IV

Concentration of salicylic acid	Ratio of salicylic acid: chrome	Gelling time
0.024 M	2 : 1	4 hours
0.040 M	3.5 : 1	30 hours
0.056 M	5 : 1	132±32 hours
0.080 M	7 : 1	200±12 hours

Example 5

Use of the crosslinking and gel-retarding system:

$\text{Cr}(\text{acetate})_3 \cdot n$ ascorbic acid

with n comprised within the range of from 0.7 to 7.

20 By operating as in the preceding Examples, aqueous, gellable compositions are prepared with a pH value of 5 ± 0.1 , which contains 5,000 ppm (par per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea and 600 ppm of trivalent chrome.

In this example, the aqueous solution of $\text{Cr}(\text{acetate})_3 \cdot \text{H}_2\text{O}$ complex is used 1 day after its preparation.

The concentration of the ligand L' (ascorbic acid) in the composition is varied within the range of from 0.008 to 0.080 M, so as to have molar ratios of ascorbic acid/chrome comprised within the range of from 0.7:1 to 7:1.

10 The so prepared compositions are submitted to gelation by being kept in an oil bath at 120°C for 15 minutes, and being then charged to an oven at 120°C . The so obtained gelling times are reported in following Table V.

Table V

Concentration of ascorbic acid	Ratio of ascorbic acid: chrome	Gelling time
0.008 M	0.7 : 1	2 hours
0.024 M	2 : 1	112±33 hours
0.040 M	3.5 : 1	112±33 hours
0.056 M	5 : 1	159±8 hours
0.080 M	7 : 1	278±32 hours

The tests are repeated by using an aqueous solution of $\text{Cr}(\text{acetate})_3 \cdot \text{H}_2\text{O}$ complex, aged for 1 month. The results are reported in following Table VI.

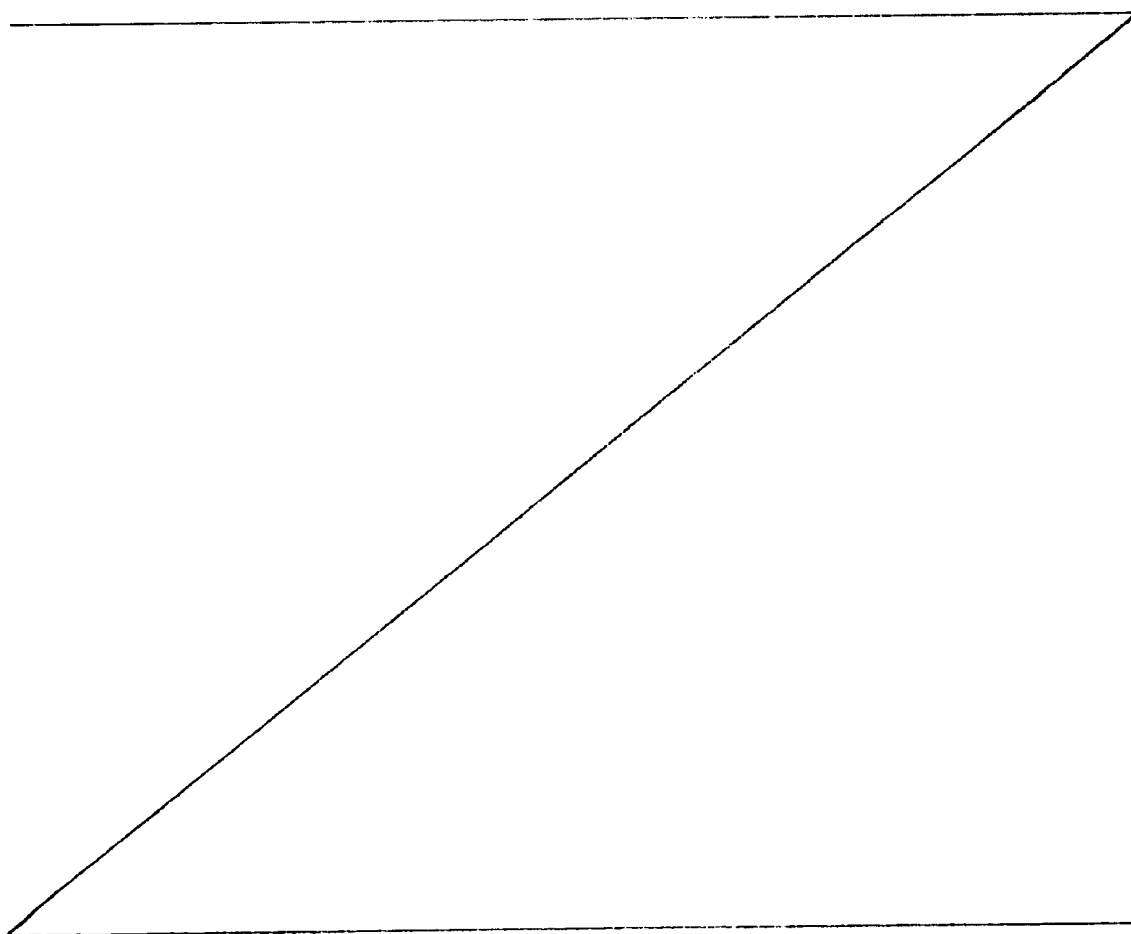
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Table VI

Concentration of ascorbic acid	Ratio of ascorbic acid: chrome	Gelling time
0.024 M	2 : 1	2 hours
0.040 M	3.5 : 1	5±1 hours
0.056 M	5 : 1	7-22 hours
0.080 M	7 : 1	54 hours
0.160 M	14 : 1	10±2 days
0.240 m	30 : 1	17±2 days

Example 6

Use of the crosslinking and gel-retarding system:



$\text{Cr}(\text{malonate})_3 \cdot n \text{ salicylic acid}$

with n comprised within the range of from 2 to 6.

By operating as in the preceding Examples, aqueous, gellable compositions are prepared with a pH value of 5 ± 0.1 , which contain 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea and 200 ppm of trivalent chrome.

The $\text{Cr}(\text{malonate})_3$ complex is prepared as described in Inorganic Syntheses, "Malonate Complexes of Chromium-(III)".

The concentration of the ligand L' (salicylic acid) in the composition is varied within the range of from 0.008 to 0.024 M, so as to have molar ratios of salicylic acid/chrome comprised within the range of from 2:1 to 6:1. For comparison purposes, a test without the ligand L' is carried out.

The so prepared compositions are submitted to gelation by being kept in an oil bath at 120°C for 15 minutes, and being then charged to an oven at 120°C . The so obtained gelling times are reported in following Table VII.

Table VII

Concentration of salicylic acid	Ratio of salicylic acid : chrome	Gelling time
0	--	15±8 hours
0.008 M	2 : 1	48 hours
0.024 M	6 : 1	150-165 hours

The tests are repeated by using $\text{Cr}(\text{malonate})_2 \cdot n$ salicylic acid as the retardant crosslinking system. The results are reported in following Table VIII.

Table VIII

Concentration of salicylic acid	Ration of salicylic acid: chrome	Gelling time
0	--	26.5 hours
0.008 M	2 : 1	55-69 hours
0.024 M	6 : 1	149-165 hours
0.080 M	20 : 1	9 days
0.160 M	40 : 1	14±1 days

Example 7

Use of the crosslinking and gel-retarding system:

$\text{Cr}(\text{glycolate})_3 \cdot n$ malonic acid

with n comprised within the range of from 2 to 10.

By operating as in the preceding Examples, aqueous, gellable compositions are prepared with a pH value of 5 ± 0.1 , which contain 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea and 200 ppm of trivalent chrome.

10 The $\text{Cr}(\text{glycolate})_3$ complex is prepared by using the procedure as described in Inorganic Syntheses, Volume 16, pages 80-81, for the preparation of complexes of Cr-(III) with malonate.

The concentration of the ligand L' (malonic acid) in the composition is varied within the range of from 0.008 to 0.04 M, so as to have molar ratios of malonic acid/chrome comprised within the range of from 2:1 to 10:1.

20 The so prepared compositions are submitted to gelation by being kept in an oil bath at 120°C for 15 minutes, and being then charged to an oven at 120°C . The so obtained gelling times are reported in following Table IX.

Table IX

Concentration	Ratio of malonic
---------------	------------------

of malonic acid	acid : chrome	Gelling time
0.008 M	2 : 1	5.5-21 hours
0.024 M	6 : 1	61-85 hours
0.04 M	10 : 1	94 hours

5

Example 8

By operating as in the preceding Examples, an aqueous, gellable composition with a pH value of 5 ± 0.1 is prepared, which contains 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea, 600 ppm of trivalent chrome [supplied as aqueous, one-month-aged $\text{Cr}(\text{acetate})_3$], and 0.024 M ascorbic acid (molar ratio of ascorbic acid to Cr = 6:1).

10

The gelation time of this composition, at 90°C , is of 23 ± 1 hours.

15

Example 9

By operating as in the preceding Examples, an aqueous, gellable composition with a pH value of 5 ± 0.1 is prepared, which contains 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea, 600 ppm of trivalent chrome [supplied as aqueous, one-month-aged $\text{Cr}(\text{acetate})_3$], and 0.024 M glycolic acid (molar ratio of glycolic acid to Cr = 2:1).

20

The gelation time of this composition, at 90°C , is of 48-50 hours.

25

Example 10

By operating as in the preceding Examples, aqueous, gellable compositions with a pH value of 5 ± 0.1 are prepared, which contain 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea, 400 ppm of trivalent chrome [supplied as aqueous, about-one-month-aged $\text{Cr}(\text{acetate})_3$], and variable

30

amounts of malonic acid.

These compositions are submitted to gelling at 120°C and in the chart of Figure 1 (----- line) the gelling time is reported as days (on the ordinate), as a function of the molar concentration of malonic acid (on the abscissa).

For comparison purposes, compositions are prepared, which are very similar to the preceding compositions, with the difference that the crosslinking and
10 gel-retarding system is constituted by Cr(acetate)₃ and acetic acid with variable amounts of the latter.

The data relevant to the gelation at 120°C are reported in the chart of Figure 1 (line -----).

Example 11

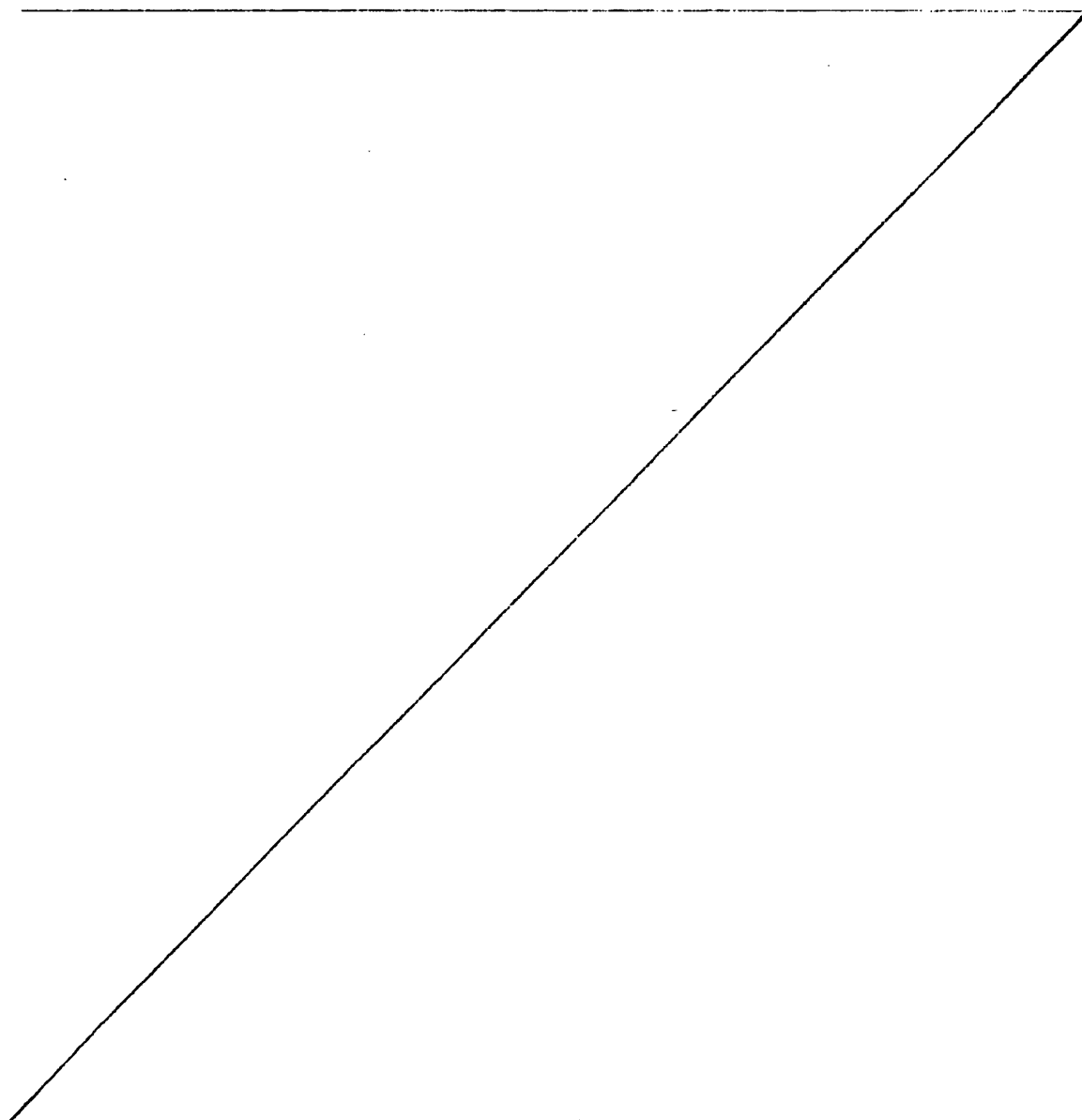
By operating as in the preceding Examples, aqueous, gellable compositions are prepared with a pH value of 5±0.1, which contain 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea and 600 ppm of trivalent chrome, supplied as
20 aqueous Cr(acetate)₃ aged for variable times, and salicylic acid in variable amounts.

The compositions are gelled at 120°C, and the results of this test are summarized in following Table X.

Table X

20a

Molar concentration of salicylic acid	Ageing time of the solution of Cr(acetate) ₃	Gelling time
0	15 minutes	< 15 minutes
0.08 M	15 minutes	< 15 minutes
0.024 M	4 hours	2 hours
0.040 M	30 hours	4 hours



0.056 M	132 hours	22 hours
0.080 M	200 hours	62 hours
0.160 M	--	118 hours

Example 12

5 By operating as in the preceding Examples, aqueous, gellable compositions are prepared with a pH value of 5 ± 0.1 , which contain 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of thiourea and 600 ppm of trivalent chrome, supplied as
 10 aqueous, fresh or 24-days-aged $\text{Cr}(\text{acetate})_3$, and salicylic acid in variable amounts.

The compositions are gelled at 120°C , and the results are reported in the chart in Figure 2.

15 In this figure, the values of molar concentration of salicylic acid in the gellable composition are reported on the abscissa, and on the ordinate the gelation time is reported as hours. In this chart, the "—" line relates to the compositions which use freshly-prepared chrome acetate and the "-----" line relates to the
 20 compositions which use 24-hours-aged chrome acetate.

Example 13

By operating as in the preceding Examples, aqueous, gellable compositions are prepared with a pH value of 5 ± 0.1 , which contain 5,000 ppm (parts per million parts by weight) of the copolymer of Example 1, 5,000 ppm of
 25 thiourea and 200 ppm of trivalent chrome, supplied as aqueous $\text{Cr}(\text{malonate})_3$, and glycolic acid in variable amounts.

The compositions are gelled at 90°C and 120°C , and the results
 30 are summarized in following Table XI.

Table XI

22.

	Molar concentration of glycolic acid---	Gelling time at 20°C-----	Gelling time at 120°C-----
5	0.008 M	117-141 hours	29-47 hours
	0.024 M	284-308 hours	47-55 hours
	0.040 M	429-453 hours	77-142 hours
	0.056 M	n.d.	142-166 hours
	0.080 M	868-933 hours	310-334 hours
	0.160 M	n.d.	343-359 hours
10	n.d. = not determined.		

Example 14

The process is carried out as in Example 13, using 20,000 ppm (parts per million parts by weight) of copolymer of Example 1, and replacing water with synthetic sea water.

The results are reported in following Table XII.

Table XII

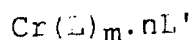
	Molar concentration of glycolic acid---	Gelling time at 20°C-----	Gelling time at 120°C-----
20	0.008 M	18-42 hours	22-46 hours
	0.024 M	72-137 hours	n.d.
	0.040 M	72-137 hours	53-118 hours
	0.080 M	309-333 hours	n.d.
	0.160 M	356-380 hours	166-190 hours
25	0.240 M	549-573 hours	290-317 hours
	0.300 M	716-740 hours	382-406 hours

n.d. = not determined.

30

CLAIMS

1. An aqueous gellable composition, containing an organic, water-soluble polymer crosslinkable with chrome ion and a crosslinking and gel-retarding system definable by the formula:



L' being in form not complexed with chrome ion
wherein:

Cr is a trivalent chrome ion;

10 L is an organic ligand consisting of a monocarboxylate or dicarboxylate ion, optionally bearing one or more amino or hydroxy functional group(s), in form complexed with chrome ion;

L' is an organic ligand selected among malonic and ascorbic acids or when L' is salicylic acid, L is selected among: acetate, propionate, butyrate, malonate, succinate, glutarate, adipate, glycolate, lactate, alpha-hydroxybutyrate, ascorbate, tartrate, alpha-aminoacetate (glycine) and alpha-amino-beta-hydroxypropionate (serine), alpha-aminobutyrate, phthalate; in form complexed with chromium ion;

20 m has a value comprised within the range of from 1 to 3, depending on the nature of the ligand L;

n has a value comprised within the range of from 0.5 to 100;

with the proviso that in the crosslinking/retardant system, the ligand L is different from the ligand L'.

2. The composition according to claim 1, characterized in that in the crosslinking and gel-retarding system, the molar ratio of the ligand L' to chrome is comprised within the range of from 0.5:1 to 50:1.

3. The composition according to claim 1, characterized in that the concentration of chrome ion in the composition is comprised within the range of from 10 to 5,000 ppm.

4. The composition according to claim 3,
10 characterized in that the concentration is comprised within the range of from 25 to 300 ppm.

5. The composition according to claims 3 and 4, characterized in that the concentration is comprised within the range of from 100 to 600 ppm.

6. The composition according to claim 1, characterized in that the concentration of the water-soluble organic polymer is comprised within the range of from 1,000 to 80,000 ppm, when salt water is used.

7. The composition according to claim 6,
20 characterized in that the concentration is comprised within the range of 3,000 to 50,000 ppm when salt water is used.

8. The composition according to claim 6, characterized in that the concentration is comprised within the range of 5,000 to 10,000 ppm when salt water is used.

9. The composition according to claim 1, characterized in that said ligands L and L' of the

crosslinking and gel-retarding system are selected from among:

- monocarboxy aliphatic acids $R\text{-COOH}$, wherein R is a $C_1\text{-}C_6$ alkyl radical;
- dicarboxy aliphatic acids $\text{HOOC-(CH}_2\text{)}_a\text{-COOH}$, wherein a has a value comprised within the range of from 0 to 4, and relevant monoesters and monoamides;
- aliphatic alpha-hydroxyacids $R'\text{-CH(OH)-COOH}$, in which R' is a hydrogen atom, or an alkyl or hydroxyalkyl radical containing from 1 to 6 carbon atoms in its alkyl or hydroxyalkyl moiety, and the lactones thereof;
- aliphatic alpha-aminoacids $R''\text{-CH(NH}_2\text{)-COOH}$, wherein R'' is a hydrogen atom, or an alkyl or hydroxyalkyl radical containing from 1 to 6 carbon atoms in its alkyl or hydroxyalkyl moiety;
- aromatic alpha-dicarboxy acids; and
- aromatic alpha-hydroxyacids.

10. The composition according to claim 9, characterized in that said ligands L and L' are: acetic acid, propionic acid and butyric acid; malonic acid, succinic acid, glutaric acid and adipic acid; glycolic acid, lactic acid, alpha-hydroxybutyric acid, ascorbic acid and tartaric acid; glycine, alpha-aminobutyric acid and serine; phthalic acid; and salicylic acid.

11. The composition according to claim 10, characterized in that the ligand L is acetate or malonate or glycolate ion and the ligand L' is selected from among: malonic acid, ascorbic acid, glycolic acid, alpha-

hydroxybutyric acid, alpha-aminobutyric acid, serine, phthalic acid and monoamide of glutaric acid.

12. The composition according to claim 11, characterized in that said crosslinking and gel-retarding system is selected from among:

- $\text{Cr}(\text{acetate})_3 \cdot n$ malonic acid,
with n comprised within the range of from 0.5 to 100;
- $\text{Cr}(\text{acetate})_3 \cdot n$ salycilic acid,
with n comprised within the range of from 0.5 to 50;
- 10 - $\text{Cr}(\text{acetate})_3 \cdot n$ ascorbic acid,
with n comprised within the range of from 0.5 to 100;
- $\text{Cr}(\text{maionate})_3 \cdot n$ salycilic acid,
with n comprised within the range of from 0.5 to 50; and
- $\text{Cr}(\text{glycolate})_3 \cdot n$ malonic acid,
with n comprised within the range of from 0.5 to 100;
- $\text{Cr}(\text{malonate})_3 \cdot n$ glycolic acid,
with n comprised within the range of from 0.5 to 100.

13. The composition according to claim 1, characterized in that the crosslinking and gel-retarding
20 system additionally contains one or more hydroxy ions and/or neutral molecules and other monovalent and divalent inorganic ions, suitable for balancing the charge of the same system.

14. The composition according to claim 13, wherein the neutral molecules is water or pyridine.

15. The composition according to claim 13, wherein the monovalent inorganic ions are Na^+ and K^+ .

16. The composition according to claim 1, characterized in that said organic polymer is selected from the group consisting of acrylamide homopolymers and acrylamide copolymers with one or more copolymerisable unsaturated monomer(s) selected from the group consisting of acrylic acid, methacrylamide, sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone, which acrylamide homopolymers or copolymers have a molecular weight comprised within the range of from 100,000 to 20,000,000, and preferably of from 200,000 to 12,000,000, said acrylamide homopolymers and copolymers being substantially non-hydrolysed (less than 1% of amidic groups hydrolysed into free carboxy groups), or partially hydrolysed (more than 1% of amidic groups hydrolysed into free carboxy groups).

17. The composition according to claim 15, characterized in that the copolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate, the copolymers of acrylamide with N-vinyl-2-pyrrolidone and the terpolymers of acrylamide with sodium 2-acrylamido-2-methyl-propane-sulfonate and N-vinyl-2-pyrrolidone are used.

18. The composition according to claim 1, characterized in that it additionally contains one or more stabilizer agent(s) for the polymer.

19. The composition according to claim 17, wherein the stabilizer agent is thiourea.

20. The composition according to claim 1, characterized in that it has a pH value comprised within the range of from about 2 to about 9.

21. The composition according to claim 19, wherein the pH value is within the range of from about 4 to 7.

22. Process for reducing the permeability in a petroleum reservoir, which process comprises the following steps:

- 10 (a) preparing an aqueous gellable composition as claimed in claim 1;
 - (b) injecting said gellable composition into the petroleum reservoir through at least one well;
 - (c) causing said composition to flow through the reservoir, until it reaches and substantially fills the high-permeability region which has to be treated; and
 - (d) causing said composition to turn into a gel, with the permeability of the above said region being
- 20 consequently decreased.

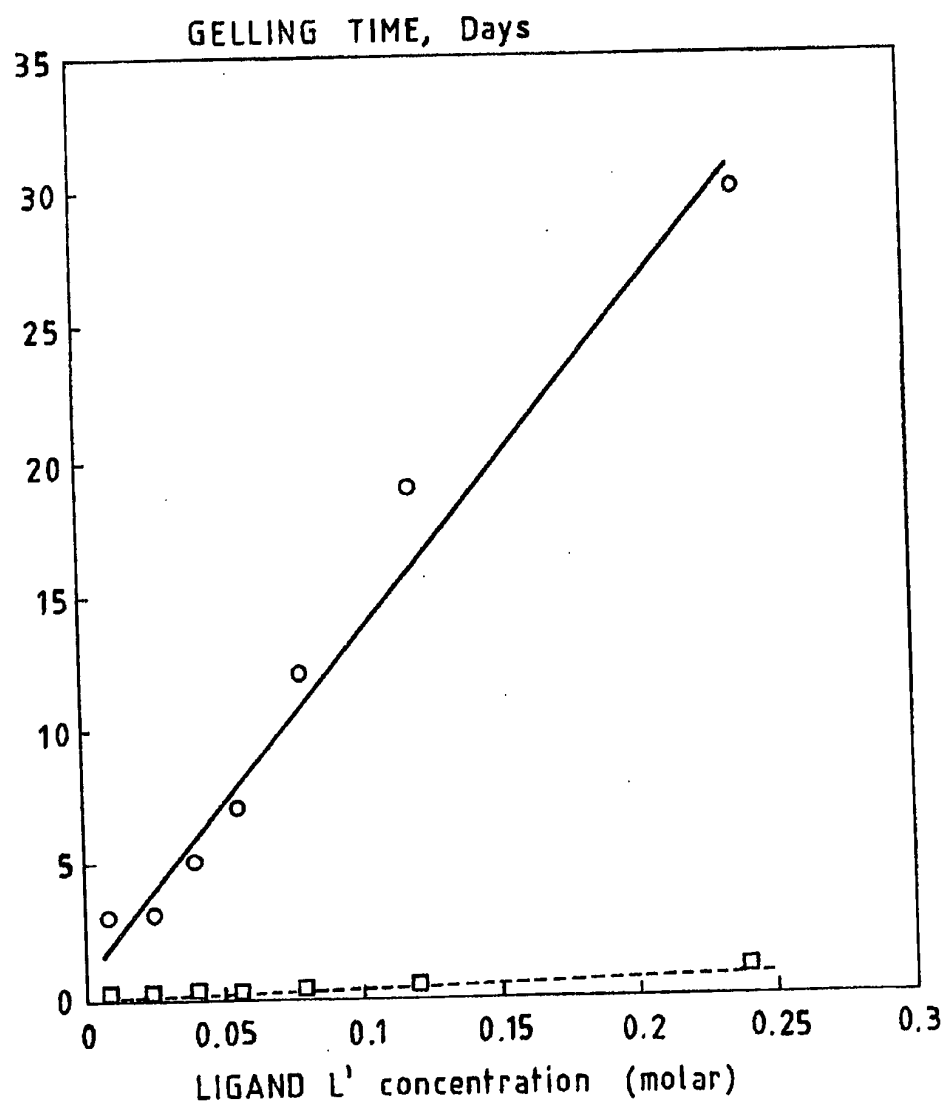
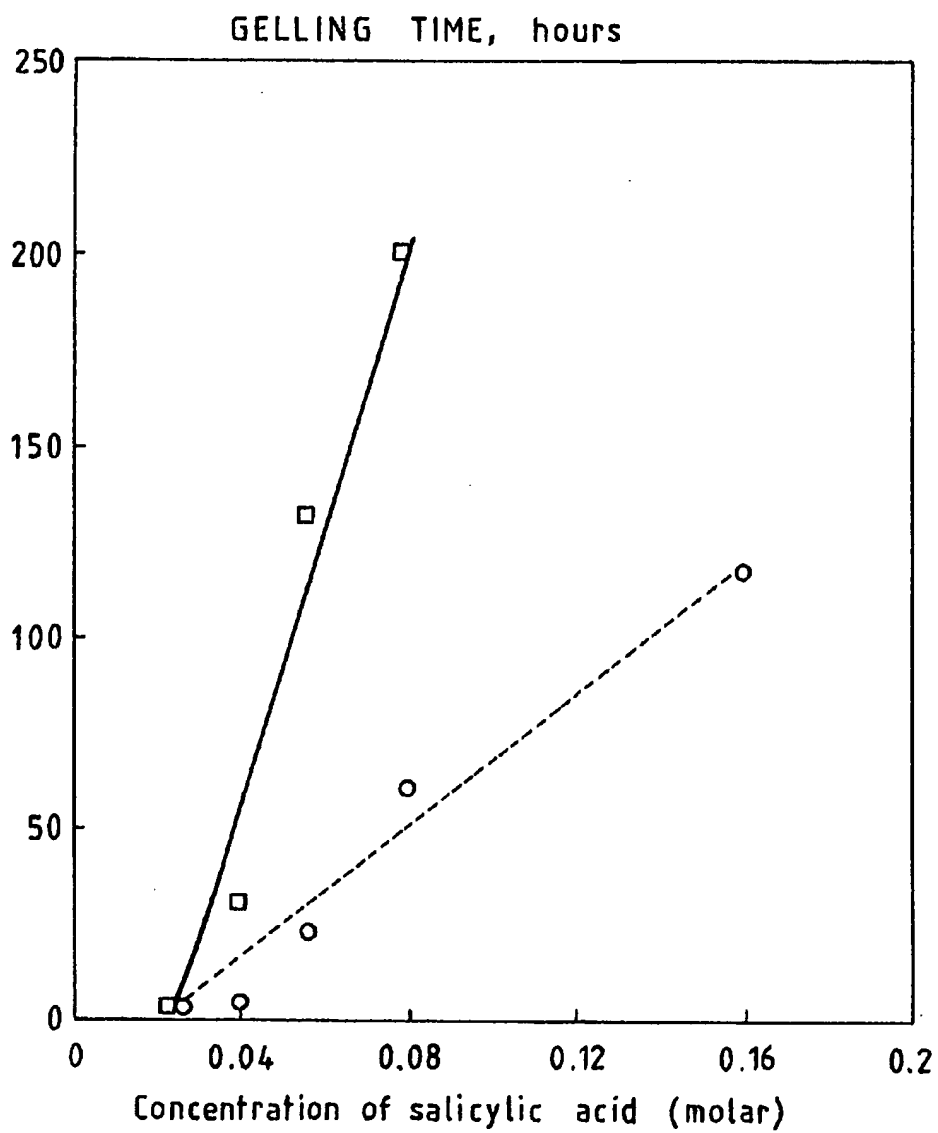
Fig.1

Fig.2

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